Integrated Ceramic Membrane System for Hydrogen Production

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Objectives

- Develop an integrated ceramic membrane system using an oxygen transport membrane (OTM) in the first stage to produce syngas and a hydrogen transport membrane (HTM) in the second stage to produce hydrogen at a low cost on a scale of 1000-5000 SCFH
- Develop a palladium-based HTM that can meet performance goals for flux, selectivity, life, and cycling on a bench scale
- Develop the substrate materials, coating materials, and appropriate manufacturing technology
- Confirm membrane performance under simulated reactor conditions
- Confirm that the process is cost competitive for distributed hydrogen production

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- A. Fuel Processor Capital Costs
- E. Control and Safety
- Z. Catalysts
- AA.Oxygen Separation Technology
- AB.Hydrogen Separation and Purification

Approach

- Update literature review
- Develop substrate
- Develop membrane
- Confirm membrane performance through tube testing
- Update process economics

Accomplishments

- Completed Phase I
- Determined that the two-stage integrated ceramic membrane process could be cost competitive if the membranes can be developed

- Identified alloy compositions with suitable resistance to contaminants
- Identified substrate compositions with suitable thermal expansion properties
- Fabricated porous ceramic support tubes
- Coated the porous ceramic support tubes with palladium alloy

Future Directions

- Produce leak-free composite palladium alloy membranes
- Demonstrate membrane performance in simulated reactor conditions
- Determine the cost of hydrogen production using palladium alloy membranes
- Decide whether to continue the project based on membrane performance and projected costs

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Introduction

Hydrogen can be produced from natural gas by mixing it with steam, oxygen, air, or a combination of these to produce syngas, which contains hydrogen. One potentially low cost, efficient way to produce syngas is to use a ceramic membrane to separate oxygen from air. The separated oxygen reacts with natural gas and steam over a catalyst to produce syngas. The membrane, which can be integrated into the syngas generator, eliminates the need for a large, expensive air separation plant. (The work on oxygen membranes is being done in a different project.) Implementing those membranes to produce hydrogen is one of the goals of this project. To produce hydrogen, the product syngas is typically sent to another reactor where most of the CO and some of the steam in the syngas react to produce additional hydrogen. Using conventional existing technology, the hydrogen in the product stream from the second reactor must be purified using additional large, expensive equipment. The goal of the current phase of this project is to simplify hydrogen production by combining the second reactor and the hydrogen purification into a single step in a single vessel, which could significantly reduce the cost of producing hydrogen, and consequently, reduce the price of hydrogen to the consumer. Because of the way that the reaction and separation are combined, it is also possible to produce more hydrogen than would be possible using the conventional two-step approach, providing additional benefit to the consumer.

Phase I of this project analyzed and compared several different processes. Based on projected cost, efficiency, and likelihood of success, a two-stage process wherein each stage was comprised of a membrane reactor was selected. The analysis indicated that this process has the potential to be the least expensive hydrogen production method of those evaluated. Phase II, which began earlier this year, has focused on developing the hydrogen purifier to put this process into practice. Potential materials have been identified, and several attempts have been made toward fabricating the hydrogen purifier. These attempts have shown continuous improvement and provided essential information about what remains to be done to produce an effective purifier.

Approach

The first step in developing the hydrogen purifier was to determine possible materials for the membrane based on available results in the technical literature. Some membrane compositions examined in the past have been unable to resist contamination caused by other materials in the syngas, such as CO or sulfur. Other compositions have failed because they were made of materials with different thermal expansion characteristics so that when the final membrane was heated, the layers separated, destroying the membrane. Possible membrane compositions that are expected to be sufficiently resistant to contaminants and not separate when heated were identified.

The next step in the project is to make and test the membrane to confirm its performance. Porous substrates using ceramic materials have been made based on our expertise in producing ceramic membranes for other applications. These substrates have been coated with palladium, and the resulting membranes have been analyzed. Controlling the pore size and porosity of the ceramic substrate is critical to ensuring that the coating will be leak free and uniform while being sufficiently thin to provide adequate performance at a reasonable cost. The porous substrates have shown continuous improvement because of improved techniques designed to control the pore size and porosity of the substrates. Once sufficient membranes have been produced, they will be tested in a demonstration reactor using simulated syngas.

Provided that the membrane development is successful, the economic assessment performed in Phase I will be revised using the test data. If the integrated ceramic membrane process still appears to be a low-cost hydrogen generation process, we will advance to the next part of the project, which is testing the membrane in an integrated reactor.

Results

In the initial trial, eight porous ceramic tubes were fabricated by isostatic pressing. One of the tubes was activated and plated with palladium alloy layers. The tube was then thermally annealed in argon. Samples of the tube that were analyzed by scanning electron microscope (SEM) before and after annealing indicated the metal film thickness was about 4 μm. SEM analysis indicated that the top surface of this substrate tube was rough with up to 40-50 micron size holes on the surface. Although the plating appeared to go on well and seemed to follow contours into the large holes, it did not appear to bridge the gap at all of the large openings on the surface. A nitrogen leak test confirmed the presence of through holes throughout the surface, as indicated by the SEM analysis of the top surface of annealed films. Figures 1 and 2 show the top of the substrate surface before and after heating, respectively. These pictures clearly show the surface roughness and the size of large 40-50 μm size openings on the surface.

Because of the problems with these tubes, the next group of tubes was made with smaller pores, and thicker plating was used, as shown in Figures 3 and 4. Each of these steps was expected to improve the tube and make it less likely to leak. Tube # 030327-0 was activated and plated with palladium

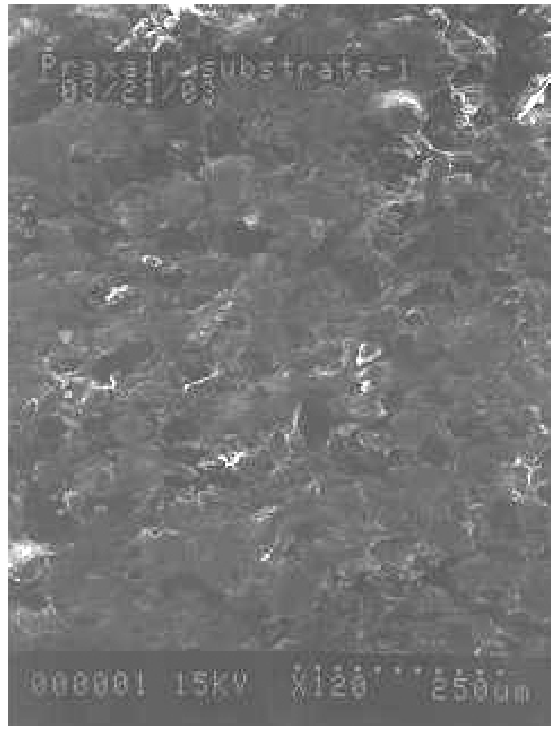

Figure 1. Schematic of Fabricated Tri-layer

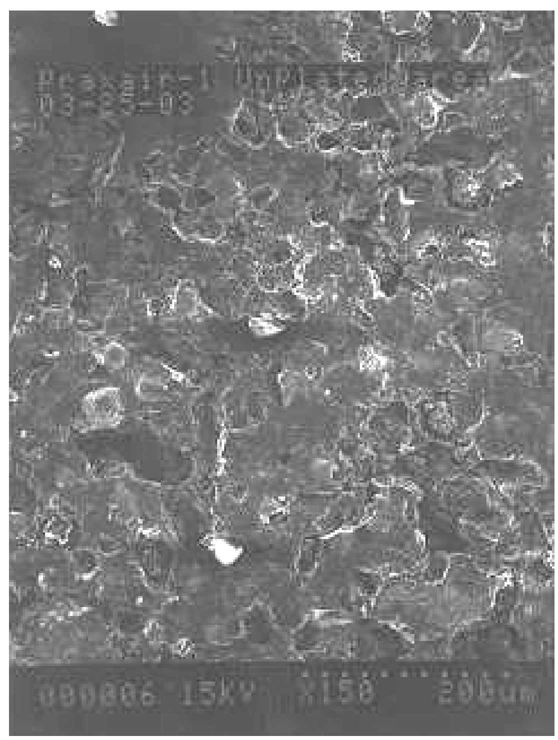

Figure 2. Top of Surface after Annealing

alloy. However, permeation analysis indicated a substantial leak of nitrogen through pinholes throughout the surface. Although the average pore size of the openings on the surface of this tube was smaller than the pores in the first batch, with a finer surface texture, large openings of the order of 50 µm were still evident on the surface (Figure 3). Although the plating appeared to go on the surface well and followed the contours into the large holes, it still did not bridge the gap at all of the large openings on the surface, as seen in Figure 4.

This batch of tubes showed improvement over the first batch, but the substrate surface needs to be smoother with smaller, more uniform openings to obtain a leak-tight metal film. Work on developing improved substrates continues.

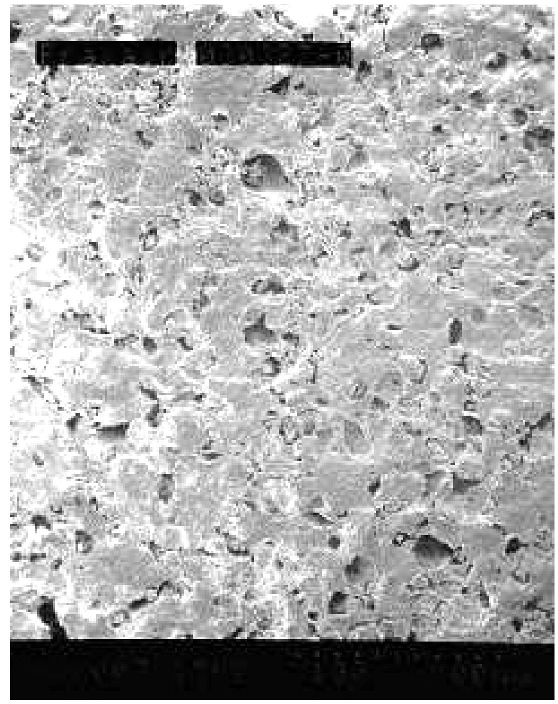

Figure 3. Top of Zirconia Substrate

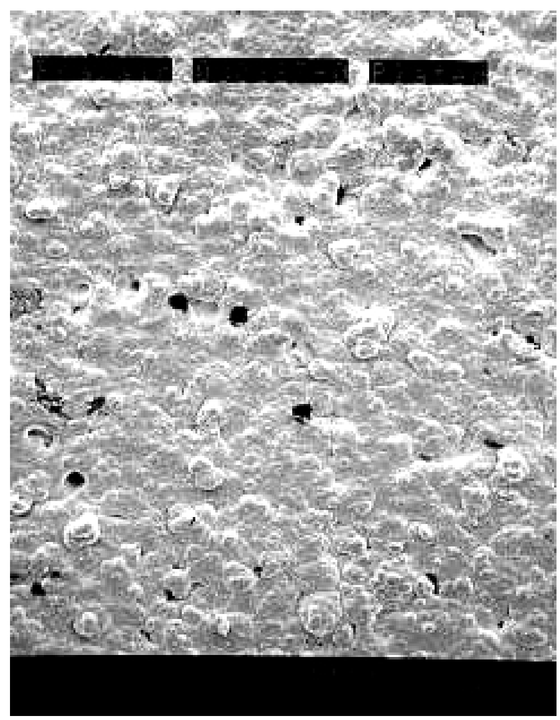

Figure 4. Top of Surface After Plating

Conclusions

- Palladium alloy compositions exist that have sufficient hydrogen flux and resistance to possible contaminants, such as sulfur and CO.
- Low-cost substrate materials exist with proper thermal expansion properties so that thermal cycling of the final membrane is likely to be possible.
- These substrate materials can be fabricated into porous tubes and coated with palladium alloy.
- Control of substrate pore size and porosity is critical.

FY 2003 Publications/Presentations

1. Presentation at the DOE Annual Merit Review Meeting

2. Semi-Annual Progress Report submitted to DOE